SPECTROSCOPIA MOLECULAR

Un bulletin mensual de novas e informationes de interesse e valor al spectroscopistas molecular

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CONSTANTES ROTATIONAL DE GeH_3D e $GeHD_3$

(Summario de un articulo submittite al J. Chem. Phys. le 26 de martio 1954.)

IE ANALYSE del structura rotational del fundamental de tension Ge-H in GeH_3D dava:

$$B'' = 1,95_7,\ B'' - B' = 0,014_2 \pm 0,0017,$$

$$e\ \sigma_0 = 1520,4 \pm 0,2\ K.$$

Un simile analyse del modo de tension Ge-H in GeD_3H dava:

$$B'' = 1,665,\qquad B'' - B' = 0,012_8,$$

$$e\ \sigma_0 = 2112,4 \pm 0,2\ K.$$

Le distantia Ge-H obtenite sub le supposition que ille remane incambiate per le substitution isotope es $1,52_0 \pm 0,003$ e $1,525 \pm 0,005$ A in GeH_3D e $GeHD_3$, respectivemente.

LOUIS P. LINDEMAN
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METHANOS SUBSTITUITE. XXII. SPECTROS INFRARUBIE DE $CHBrF_2$ E CONSTANTES DE ENERGIA POTENTIAL E PROPRIETATES THERMODYNAMIC DE $CHBrF_2$ E $CDBrF_2$

(Summario de un articulo submittite al J. Chem. Phys. le 20 de maio 1954.)

IE ANALYSE del presente e previe datos spectral infrarubie de $CHBrF_2$ in conjunction con le tractamentos del coordinatas normal de $CHBrF_2$ e $CDBrF_2$ dava le sequente numeros de undas fundamental:

Fundamental	$CHBrF_2$	$CDBrF_2$
$\sigma_1(a')$	3003 K	2208

(continuate al pagina 40)

SPECTRO MICROUNDIC E STRUCTURA DE BENZONITRILO

(Summario de un articulo submittite al J. Chem. Phys. le 15 de april 1954.)

IE spectro rotational de benzonitrilo ha essite studiate in le region de $\lambda = 1$ cm, e circa 20 lineas de absorption ha essite correlatate con le theoria del rotor rigide asymmetric. Le momentos principal de inertia es 89,370, 326,740, e 416,183 upa A^2 (unitates de peso atomic-angstrom^2). Le evidentia indica un structura planari symmetric con le dimensiones del anulo essentialmente le mesme como in benzina. Le momento dipolic es 4,14 ± 0,05 D (unitates Debye).

DAVID R. LIDE, JR.

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NOS considera iste veritates como obvie: que omne homines es create equal, que illes es dotate per lor Creator con certe derectos inalienable, que inter illos es vita, libertate, e le persequita de felicitate. -- Que, pro assecurar iste derectos, governamentos es instituite inter le homines, derivante lor juste potentias ab le consentimento del governato, -- Que, quandocunque alicun forma de governmento deveni destructive de iste fines, il es le derecto del populo cambiar o abolir lo e instituer un nove governamento, establiente su fundamento super tal principios e organisante su potentias in un tal forma, que a illes pare le plus apte a effectuar lor securitate e felicitate.

-- Ex le DECLARATION DE INDEPENDENTIA del Statos Unite de America, le 4 de julio 1776.

TRACTAMENTOS DEL COORDINATAS NORMAL DE MOLECULAS POLYATOMIC

Salvador M. Ferigle e Alfons Weber
Instituto Technologic de Illinois, Chicago 16, Illinois
(continuate ab Spec. Mol. 3, 33 (1954))

4.0 USO DE SYMMETRIA

4.1 Introduction. Le tractamento del coordinatas normal de un molecula polyatomic es essentialmente un problema del eigenvalores e eigenvectores. Le equation secular de un tal problema pote esser simplificate per le uso de methodos del theoria de gruppos. Le objectivo es trovar un collection de si-nominate coordinatas de symmetria le quales forma le base de un completemente reducite representation del gruppo de symmetria molecular. Isto duce a un complete factorar del equation secular le qual es possibile a causa del invariantia del energias cinetic e potential sub omne le operationes del gruppo punctic del molecula, e reimplacia un equation de alte grado per plure equationes de grado plus basse.

Le problema de vibrationes molecular pote esser studiate in plure manieras:

1) Per le uso de 3N coordinatas cartesian le quales describe le parve displaciamentos del N nucleos atomic ab le configuration de equilibrio. Tunc 3N coordinatas de symmetria es formate e le complete equation secular ha sex radices que es equal a zero. Istos corresponde al translationes e rotationes del molecula.

2) Per uso de 3N coordinatas cartesian de displaciamento, le conditiones Eckart es prendite in conto e 3N - 6 grados de libertate vibrational remane. Tunc 3N - 6 coordinatas de symmetria es formate.

3) Per le uso de 3N - 6 coordinatas interne, consistente con le conditiones Eckart, e tunc per formar le mesme numero de coordinatas de symmetria.

Un molecula es un systema que es mechanicamente stabile, i.e. illo possede un configuration de equilibrio. In iste configuration de equilibrio, le nucleos es locate a positiones fixate con respecto le unes al alteres. Il ha un numero definite de operationes geometric, nominate operationes de coperir, le quales pote esser facite in le molecula si que nucleos equivalente occupa le mesme punctos in spatia como in le configuration de equilibrio initial. Il ha solmente duo typos de operationes de coperir: rotationes proprie e rotationes improprie. Un rotation proprie es simplemente un rotation per un angulo ϕ circa un axe de symmetria. Un rotation improprie es un rotation sequite per un reflexion in un plano perpendicular al axe de rotation. Assi un reflexion es un rotation improprie per un angulo de 0°. Omne le operationes de coperir que pote esser facite super un molecula forma un gruppo G. On dice que le molecula pertine al gruppo G o ha le symmetria G.

Certe ligamines e angulos interligaminic es etiam permutate le unes in le alteres per le operationes de G, e le coordinatas interne es transformate similemente. Date un coordinata interne, omne le coordinatas interne in le quales illo es transformate per le operationes de symmetria de G es nominate coordinatas interne equivalente. Seligente 3N - 6 coordinatas interne, cata operation de G transforme los le unes in le alteres e le collection de matrices quadrate correspondente a iste transformationes pro omne le elementos de G forma un representation reducibile de G. Le matrices de iste representation forma semper blocos a transverso le diagonal principal, al minus al extento que es necessari pro separar le collectiones de coordinatas interne equivalente. Le collectiones de iste matrices de ordine plus basse correspondente al coordinatas interne equivalente etiam forma representationes reducibile de G.

Le problema es reducer iste representation. Le transformation a coordinatas de symmetria ducente a iste reduction etiam reduce le matrices del energia cinetic e potential a causa del invariantia de illos sub le operationes de G.

Le selection del combinationes linear del coordinatas elementari -- cartesian o interne -- esseva al comenciamente un cosa de experientia e intuition. Nielsen e Berryman[10] recentemente ha date un procedura analytic pro trovar le coordinatas

de symmetria. Iste methodo es basate super le algebra de representationes de gruppo.[18]

---

[18] Vide E. Wigner, Gruppentheorie und ihre Anwendung auf die Quantenmechanik der Atomspektren (Friedich Vieweg und Sohn, Braunschweig, 1931), capitulo 12.

4.2 Algebra de representationes de Gruppo. Lassa nos considerar un gruppo de ordine h e lassa R denotar alicun del operationes del gruppo. Lassa $D^j(R)$ esser un irreducibile representation unitari de dimension l_j.

On dice que un collection de functiones f_i^j ($i = 1, 2, \dots, l_j$), si seligite que

$$Rf_i^j = \sum_{k=1}^{l_j} D^j(R)_{ki}\, f_k^j \qquad (54)$$

es valide pro omne le operationes del gruppo, pertine al representation irreducibile $D^j(R)$. On etiam dice que le function f_i^j pertine al linea i del representation irreducibile $D^j(R)$. Il es bencognoscite que representationes irreducibile es determinate solmente usque a un transformation de similaritate arbitrari. Nonobstante, le previe definition de f_i^j como pertinente a un linea particular del representation face senso solmente si le representation irreducibile es completemente determinate.

Le proprietate de orthogonalitate del representationes irreducibile statue que

$$\sum_R D^j(R)_{ik}{}^* D^{j'}(R)_{i'k'} = (h/l_j)\, \delta_{jj'}\delta_{ii'}\delta_{kk'}, \qquad (55)$$

ubi le summa es prendite super omne le operationes del gruppo e le δ es le symbolos Kronecker

$$\delta_{jj'} = \begin{cases} 1 & \text{pro } j = j' \\ 0 & \text{pro } j \neq j'. \end{cases}$$

Per multiplicar Eq. 54 per $D^{j'}(R)_{k'i'}{}^*$, summar super omne le operationes del gruppo (o integrar in le caso de gruppos continue), e usar le proprietate de orthogonalitate de Eq. 55, nos obtene

$$\sum_R D^{j'}(R)_{k'i'}{}^* Rf_i^j = \sum_R \sum_k D^{j'}(R)_{k'i'}{}^* D^j(R)_{ki}\, f_k^j =$$

$$\sum_k (h/l_j)\, \delta_{jj'}\, \delta_{kk'}\, \delta_{ii'}\, f_k^j = (h/l_j)\, \delta_{jj'}\, \delta_{ii'}\, f_{k'}^j. \qquad (56)$$

Pro le casc de $j = j'$, $i = i'$, Eq. 56 da, per lassar cader le primo in k',

$$\sum_R D^j(R)_{ki}{}^* Rf_i^j = (h/l_j) f_k^j \qquad (57)$$

le qual pote esser usate pro obtener ex f_i^j le $l_j - 1$ functiones associate f_k^j.

Si nos considera $k = i$ in Eq. 57, tunc

$$\sum_R D^j(R)_{ii}{}^* Rf_i^j = (h/l_j) f_i^j \qquad (58)$$

le qual da le condition que f_i^j pertine al linea i del representation irreducibile j. Le linearitate de Eq. 58 monstra que un combination linear del functiones que pertine al linea i del representation irreducibile j etiam pertine al mesme linea del representation complete.

Alicun function F le qual pote esser operate per le elementos R pote esser findite in un summa

$$F = \sum_{j=1}^{c} \sum_{i=1}^{l_j} f_i^j, \qquad (59)$$

ubi f_i^j pertine al linea i del representation irreducibile j.

Pro obtener le functiones f_i^j in Eq. 59, nos applica R, multiplica per $D^{j'}(R)_{kk}{}^*$, e summa super omne le operationes del gruppo. Assi

$$\sum_R D^{j'}(R)_{kk}{}^* RF = \sum_{Rij} D^{j'}(R)_{kk}{}^* f_i^j = \sum_{ij} (h/l_j)\, \delta_{jj'}\, \delta_{ik}\, f_k^j = (h/l_j)\, f_k^{j'} \qquad (60)$$

le qual monstra que pro un function arbitrari F le summa

$$\sum_R D^j(R)_{kk}{}^* RF$$

pertine al linea k del representation irreducibile j.

Duo functiones que pertine al un o le altere de duo representationes irreducibile differente, o a duo lineas differente

del mesme representation, es orthogonal. Lassa le functiones esser f_i^j e $g_{i'}^{j'}$; tunc

$$(f_i^j, g_{i'}^{j'}) = (Rf_i^j, Rg_{i'}^{j'}) =$$

$$\left(\sum_{k=1}^{l_j} D^j(R)_{ki} f_k^j, \sum_{k'=1}^{l_{j'}} D^{j'}(R)_{k'i'} g_{k'}^{j'} \right)$$

$$= \sum_{k,k'} D^j(R)_{ki} * D^{j'}(R)_{k'i'} (f_k^j, g_{k'}^{j'}),$$

e per summar super omne R, on obtene

$$h(f_i^j, g_{i'}^{j'}) =$$

$$\sum_{k,k'} \delta_{jj'} \delta_{kk'} \delta_{ii'} (h/l_j)(f_k^j, g_{k'}^{j'})$$

$$= \delta_{jj'} \delta_{ii'} (h/l_j) \sum_k (f_k^j, g_k^{j'}),$$

le qual monstra que $(f_i^j, g_{i'}^{j'}) = 0$, si non $j = j'$ e $i = i'$, e etiam que (f_i^j, g_i^j) es independente de i.

—(Va continuar in un numero futur) —

METHANOS SUBSTITUITE (continuate ab p.37)

Fundamental	$CHBrF_2$	$CDBrF_2$
$\sigma_2(a')$	1280	1134
$\sigma_3(a')$	1135	1019
$\sigma_4(a')$	718	623
$\sigma_5(a')$	577	578
$\sigma_6(a')$	240[a]	240
$\sigma_7(a'')$	1344	1109
$\sigma_8(a'')$	1108	977
$\sigma_9(a'')$	323	323

[a]Determinate ab bandas de combination.

Le valores pro $CHBrF_2$ es observate, illos pro $CDBrF_2$ es calculate.

Le constantes del energia potential es:

f_b 3,30000, f_f 6,27990,

f_h 4,97680 md/A; e

f_{bf} 1,07858, f_{bh} 0,63789,

f_{ff} 2,13953, f_{fb} 0,89222 md A/rad^2.

Hic b = Br, f = F, h = H, bf = Br-C-F, etc. Valores de 27 constantes de interaction etiam es date.

Valores calculate del contento caloric, energia libere, entropia, e capacitate caloric in calorias grado^{-1} mole^{-1} es:

$CHBrF_2$

T(°K)	H/T	-F/T	S°	C_p°
100	8,26	49,93	58,19	9,21
200	9,39	55,99	65,38	11,77
273,16	10,26	59.05	69,31	13,48
298,16	10,56	59,96	70,51	14,04
300	10,57	60,02	70,59	14,08
400	11,72	63,22	74,95	16,17
500	12,79	65,95	78,74	17,87
600	13,75	68,37	82,12	19,20
700	14,61	70,56	85,17	20,24
800	15,36	72,56	87,92	21,06
900	16,03	74,41	90,44	21,72
1000	16,63	76,15	92,78	22,26

$CDBrF_2$

100	8,27	50,01	58,28	9,22
200	9,46	56,09	65,55	12,05
273.16	10,42	59,18	69,60	14,06
298.16	10,75	60,11	70,86	14,71
300	10,77	60,17	70,94	14,75
400	12,07	63,46	75,53	17,05
500	13,25	66,28	79,53	18,83
600	14,30	68,79	83,09	20,17
700	15,21	71,06	86,28	21,19
800	16,01	73,15	89,16	21,98
900	16,71	75,07	91,78	22,59
1000	17,32	76,89	94,21	23,08

$H = H^\circ - E_0^\circ$ e $F = F^\circ - E_0^\circ$.

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SUMMARIOS IN INTERLINGUA

IE Journal of Dental Medicine publica summarios in interlingua de su articulos jam depost april 1954. Iste jornal es le organo official del American Academy of Dental Medicine. Le redactor es Irving Yudkoff de New York.

In plus, le Secunde Congresso Cardiologic, le qual convenira in Washington, DC,

in septembre 1954, va publicar le summarios in su programma completemente in interlingua -- un texto de plus que cinquanta milles (50.000) parolas.

RECIPITE

Instrument News, Vol. 5, No. 3, 1954. Corporation Perkin-Elmer, Norwalk, Connecticut, Statos Unite. Paul A. Wilks, Redactor. Gratis.

Iste numero contine plure cosas de interesse a spectroscopistas infrarubie. Un editorial propone le formation de un societate infrarubie pro servir le interesses e necessitates special del spectroscopistas infrarubie, specialmente de illos qui usa le spectro infrarubie como un medio de analyse in applicationes industrial.

A Glass Spectrograph with a Plane Grating and of High Light-Gathering Power. Some of its Applications in Raman Spectroscopy. Ya. S. Bobovich e M. M. Pakhomova, Doklady Akademii Nauk SSSR 92, 947-950 (1953). Traduction in anglese. Disponibile ab le Office of Technical Services, Department of Commerce, Washington, 25, D.C., Statos Unite; Precio, 10 cents.

Le grilliage ha un area effective de 90 x 100 mm^2 con 1200 lineas/mm e un concentration de circa 70 per cento del energia in un del prime ordines in le region verde. Le dispersion del apparaturo es 42 A/mm.

Infrared Band Correlations for Some Substituted Olefins. R. E. Kitson, Research Division, E. I. du Pont de Nemours and Co., Inc., Wilmington, Delaware, Statos Unite. Anal. Chem. 25, 1470 (1953).

Spectros de plus que 100 olefinas substituite esseva mesurate, principalmente le halo- e cyano-olefinas. Le bandas de absorption correspondente al vibrationes de flexion extra le plano del hydrogeno ethylenic esseva studiate e lor positiones in tal moleculas comparate con lor position in le hydrogenos de carbon. Substitution in compositos de vinylo e vinylideno produceva pauc cambiamento in le position del banda in comparation con le hydrogenos de carbon correspondente, excepte quando le substituente esseva conjugate con le ligamine duple. In moleculas del typo trans-RHC=CHX, nonobstante, le banda esseva cambiate ab 10,36 a 10,74 μ quando le X esseva Cl o Br. Substitution in le gruppos de alkylo del structura cis-RHC=CHR' displaciava le banda ab su position in le hydrogenos de carbon (14,0 a 14,7 μ) a un valor de circa 13,3μ. Un banda acute e intense a 8,01 μ esseva trovate pro moleculas que contineva le gruppo $RR'C{=}CHCH_2Cl$. Le compositos correspondente con Br o I in loco del Cl ha bandas a 8,30 e 8,70 μ, respectivemente. Iste banda esseva cambiate a 7,94 e 8,25 in le compositos Cl e Br quando le hydrogeno ethylenic esseva reimplaciate. Per uso de iste modificationes e extensiones al assignations del banda de hydrogenos de carbon normal, il ha devenite relativemente simple establir le position e le typo del ligamine duple ethylenic ab le spectro absorptionic de un halo- o cyano-olefina incognite.

-o-

Duo physicos, un experimental, un theoric, es desirate al Universitate Alabama.

SOCIETATE DEL SPECTROSCOPISTAS MOLECULAR

Nove membros de iste societate es:

7(4-V-54). Herman B. Weissman, 3400 North Austin Avenue, Chicago, Illinois, Statos Unite.

8(11-V-54). Edgar Luscher, Applied Research Laboratories, 1 Rue du Tunnel, Lausanne, Switza.

9(14-V-54). Norman H. E. Ahlers, 8 Northfields Parade, Station Road, Hayes, Middlesex, Anglaterra.

10(21-V-54). Ernst Lippert, Departimento de Chemia, Technische Hochschule, Wiederholdstrasse 15, Stuttgart, Germania.

11(26-V-54). Dusan Hadzi, Departimento de Chemia, Universitate Ljubljana, Veselova 4, Ljubljana, Yugoslavia.

Altere spectroscopistas qui desira devenir membros debe retornar le formulario de application (pagina 19a), o scriber a:

Le Redactor, Spectroscopia Molecular
Cassa Postal 58
Instituto Technologic de Illinois
Chicago 16, Illinois, Statos Unite.

CALENDARIO DE EVENTOS SPECTROSCOPIC

Julio 1-3. Commission Juncte pro Spectroscopia, Lund, Sveda; e etiam in Lund,

Julio 1-7. Conferentia super Spectroscopia Atomic, in commemoration del nascentia de Rydberg. (P. F. A. Klinkenberg, Universitate Amsterdam, Muidergracht 4, Hollanda.)

Julio 12-23. Spectroscopia industrial moderne. Un programma designate specialmente pro chemistas e physicos ex industrias que es in le processo de installar equipamento spectrographic. (Prof. J. J. Devlin, Departimento de Physica, Collegio Boston, Chestnut Hill 67, Boston, Massachusetts, Statos Unite.

Julio 15-17. Symposio super Particulas Solide in Objectos Astronomic, Universitate Liège. (J. Duchesne, Liège, Belgica.)

Julio 19-30. Programma super spectroscopia infrarubie; instrumentation, methodos laboratorial, e solution de problemas chimic. Directores: Richard C. Lord e Foil A. Miller. (E. H. Huntress, Instituto Technologic de Massachusetts, Cambridge 39, Mass., Statos Unite.)

Augusto 30-September 3. 5te Colloquio International super Spectroscopia, Gmunden, in Austria Superior. Spectroscopia emissionic e molecular. Prof. F. X. Mayer, Chef. (J. R. Stansfield, Hilger and Watts, Ltd., 98 St. Pancras Way, London, N.W. 1, Anglaterra.)

September 3-7. Symposio International super Spectroscopia Infrarubie, Parma, Italia. Centenario de Macedonio Melloni (1798-1854). (G. Polvani, Via Saldini 50, Milano, Italia.)

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Presente numero de membros del Societate Del Spectroscopistas Molecular . . 11

SPECTROSCOPIA MOLECULAR es redigite e publicate mensualmente in interlingua per professor Forrest F. Cleveland del Laboratorio de Spectroscopia, Instituto Technologic de Illinois, Chicago 16, Illinois, Statos Unite. Manuscriptos pro publication debe esser submittite a ille adresse.

Le texto original es legite per Dr. Alexander Gode, Chef del Division de Interlingua de Science Service (80 East 11th Street, New York 3, N. Y.). Libros importante super interlingua, disponibile ab ille adresse, es Interlingua-English Dictionary, Interlingua Grammar, e Interlingua A Prime Vista.

Labor editorial es gratis. Le costo de preparation e distribution es recipite ab le spectroscopistas, bibliothecas, e companias. Le directores de publication es senioretta Joyce Carol Broling e senior Fred L. Voelz.

. . . . . .

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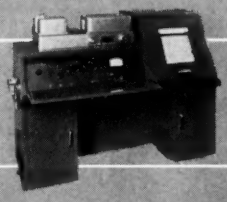

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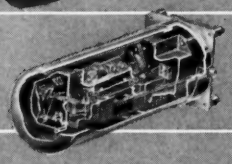

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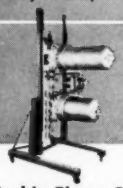

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